

HYDROGEN-OXYGEN ELECTROLYTIC REGENERATIVE FUEL CELLS

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1. INTRODUCTION

This report reviews the progress made on the development of a hydrogen-oxygen regenerative fuel cell (secondary battery) under NASA Contract NAS3-2781 during the period of 1 August through 1 September 1966. During this period, primary emphasis was placed on the testing of single cells with various electrode matrix structures in order to improve cycle life performance. Single cells tested employed variations of potassium titanatematrices to optimize fabrication techniques and to obtain performance parameters and an understanding of modes of deterioration that exist within cycling cells.

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2. TECHNICAL DISCUSSION

2.1 Single Cell Test

Nine single cell tests were conducted during this report period to evaluate various electrode and potassium titanate matrix structures. Table I is a summary of the test results and the individual cell construction variables.

During the preceding report period, testing was started on cell 206. This cell consists of an American Cyanamid type oxygen electrode and an EOS porous nickel plaque hydrogen electrode with a matrix composed of 90 percent potassium titanate and 10 percent asbestos. The American Cyanamid oxygen electrode in this cell had previously been used in cells 196 and 199. Cell 196 had been cycled 60 times and showed good initial performance, but developed slow cross gas leakage on the 60th cycle. Cell 199 was cycled continuously for 405 cycles. During the period of cycling, there was a gradual increase in charge voltage and a decrease in discharge voltage to a point in which average discharge voltage at the 405th cycle was approximately 0.5 volt. The oxygen electrode from that cell was then removed and assembled in cell 206; this cell has been cycled continuously 700 times. The voltage performance of various cycles of the cell is shown in Fig. 1. As can be seen, there is a gradual increase in the charging voltage with cycling and a gradual decrease in the discharge voltage with cycling. However, the initial performance of the cell showed that the oxygen electrode had not been permanently degraded as a result of its use in the previous cell tests. This once again points to the fact that changes in the matrix or hydrogen electrode were causing degradation in the performance observed.

SUMM

Cell	O ₂ Electrode Type Catalyst		H ₂ Electrode Type Catalyst	
206	Am. Cy.	9 mg Pt/cm ²	Plat. Nickel Plaque	20 mg Pt/cm ²
209	Plat. Nickel Plaque	20 mg Pt/cm ²	Plat. Nickel Plaque	20 mg Pt/cm ²
211	Am. Cy.	9 mg Pt/cm ²	Plat. Nickel Plaque	20 mg Pt/cm ²
212	Am. Cy.	40 mg Pt/cm ²	Plat. Nickel Plaque	20 mg Pt/cm ²
213	Am. Cy.	9 mg Pt/cm ²	Plat. Nickel Plaque	20 mg Pt/cm ²
214	Am. Cy.	9 mg Pt/cm ²	Plat. Nickel Plaque	20 mg Pt/cm ²
215	Am. Cy.	9 mg Pt/cm ²	Plat. Nickel Plaque	20 mg Pt/cm ²
216	Am. Cy.	9 mg Pt/cm ²	Am. Cy.	9 mg Pt/cm ²
217	Am. Cy.	40 mg Pt/cm ²	Plat. Nickel Plaque	20 mg Pt/cm ²

* Electrolyte, all cases: 40% KOH; 34 grams by weight

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TABLE I
ARY OF SINGLE CELL TESTS

Matrix Composition (%)	Matrix Dry Wt (grams)	Comments*	Results
90 KT 10 asbestos	20.0	O ₂ electrode used in cells 196 and 199	700 cycles. Gradual degradation
90 KT 10 asbestos	22.0	H ₂ concentration cell	Still on test, stable performance
90 KT 10 polypropylene	21.5		50 good cycles, then developed slow gas recombination
90 KT 10 asbestos	22.0		418 cycles, then developed slow recom- bination last 17 cycles
90 KT 10 polypropylene	22.0	O ₂ electrode was used in cell 211	119 cycles, then developed slow gas recombination
90 KT 10 asbestos	21.5	O ₂ electrode used in cells 196, 199, and 206	281 cycles. Still on test; good performance
90 KT 10 polypropylene	21.5	Used electrodes	30 cycles, then developed slow gas recombination
90 KT 10 polypropylene	21.5	New electrodes	80 cycles, gradual degradation; still on test
90 KT 10 asbestos	24.1	Used electrodes from cell 212	30 cycles. Good per- formance. Still in operation.

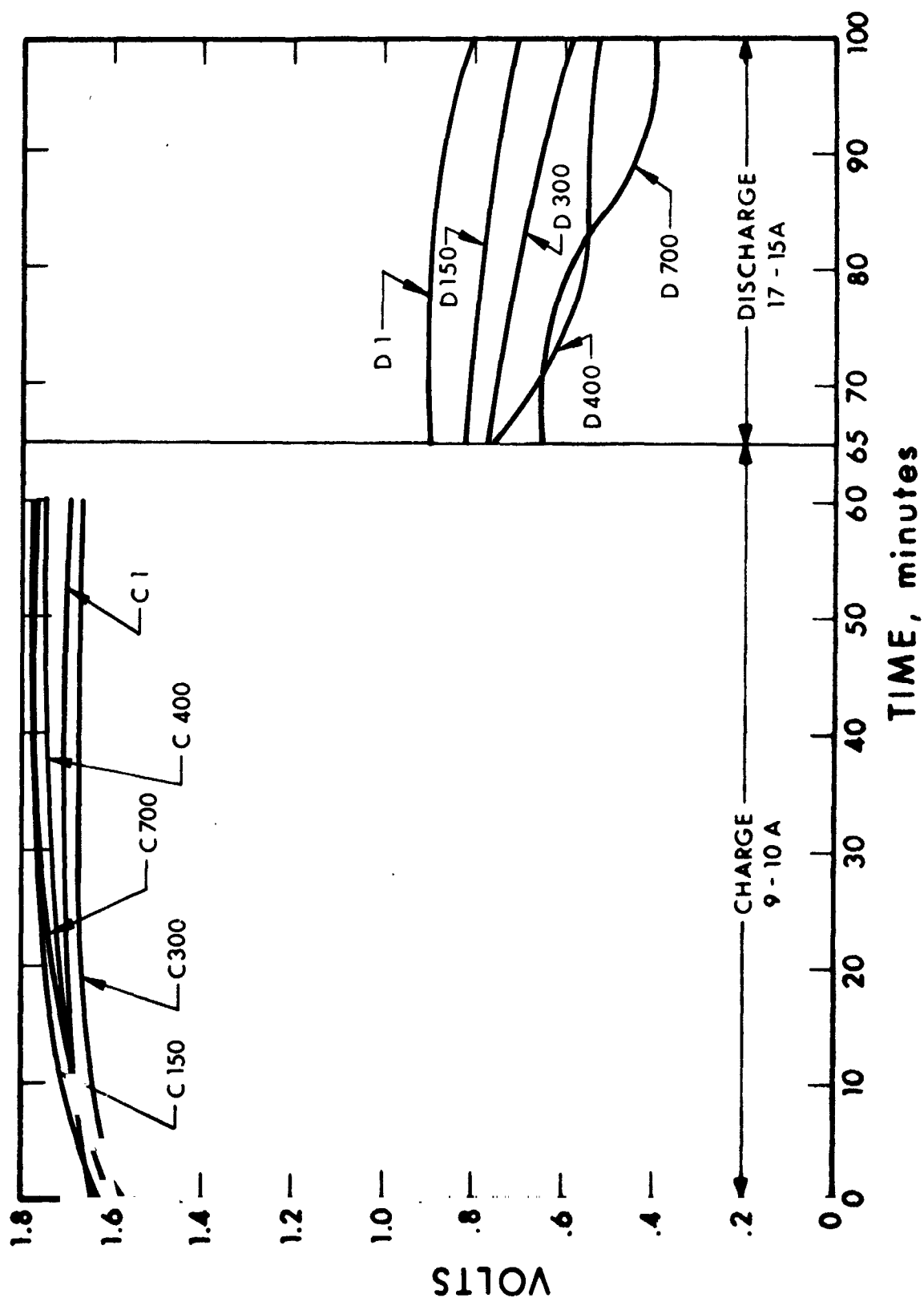


FIG. 1 CYCLING PERFORMANCE OF CELL 206

Cell 209 was a hydrogen concentration cell put on test in the previous period to determine if changes in the hydrogen electrode occur with the potassium titanate matrix. This cell consisted of two EOS porous nickel plaque hydrogen electrodes that had been chemically platinized. The voltage performance is shown in Fig. 2. As can be seen, at approximately the 500-hour point there was an increase in the voltage which leveled off again and remained relatively flat to this point (at which 1,377 hours of operation had been achieved). The results of this test seem to indicate that the hydrogen electrodes are not substantially affected by long-term use in the concentration mode.

Cell 211 consisted of an American Cyanamid oxygen electrode and a porous nickel plaque hydrogen electrode with a matrix consisting of 90 percent potassium titanate and 10 percent polypropylene fibers. The substitution of polypropylene fibers for asbestos in the mat was an attempt to eliminate asbestos (which apparently reacts gradually with the electrolyte). The cell was cycled 50 times, showing initial good voltage performance as shown in Fig. 3. Throughout the cycling of the cell, the charge and discharge voltage remained relatively stable; during the last five or so cycles, however, a slow gas recombination took place within the cell such that the cell pressure did not reach the fully charged level. On subsequent discharges there was a falloff in the discharge voltage, as shown in Fig. 3 (cycle 46). The slow gas recombination that occurred in the cell was apparently due to the structural weakness and imperfection of the matrix; thus, no conclusion could be drawn as to the ability of this type of matrix to enhance cycle life of the cell.

Cells 213 and 215 were additional attempts to use a matrix composed of 90 percent potassium titanate and 10 percent polypropylene fibers. In both cases, the oxygen electrodes were American Cyanamid type and the hydrogen electrodes were platinized nickel porous plaques. Cell 213 was cycled 82 times at which point the voltage performance was relatively stable, as shown in Fig. 4. Beyond that point, a slow gas

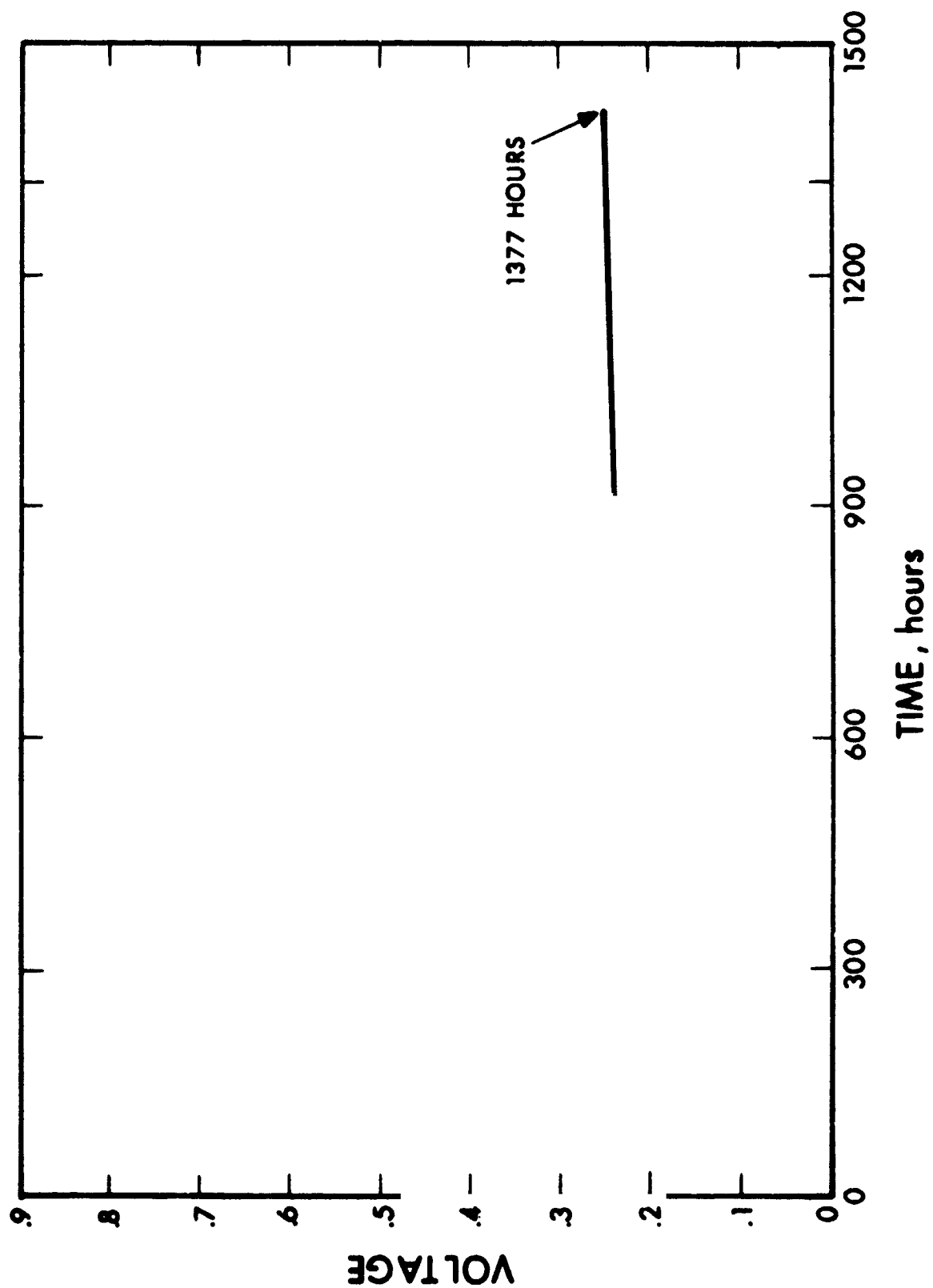


FIG. 2 P_2 CONCENTRATION CELL

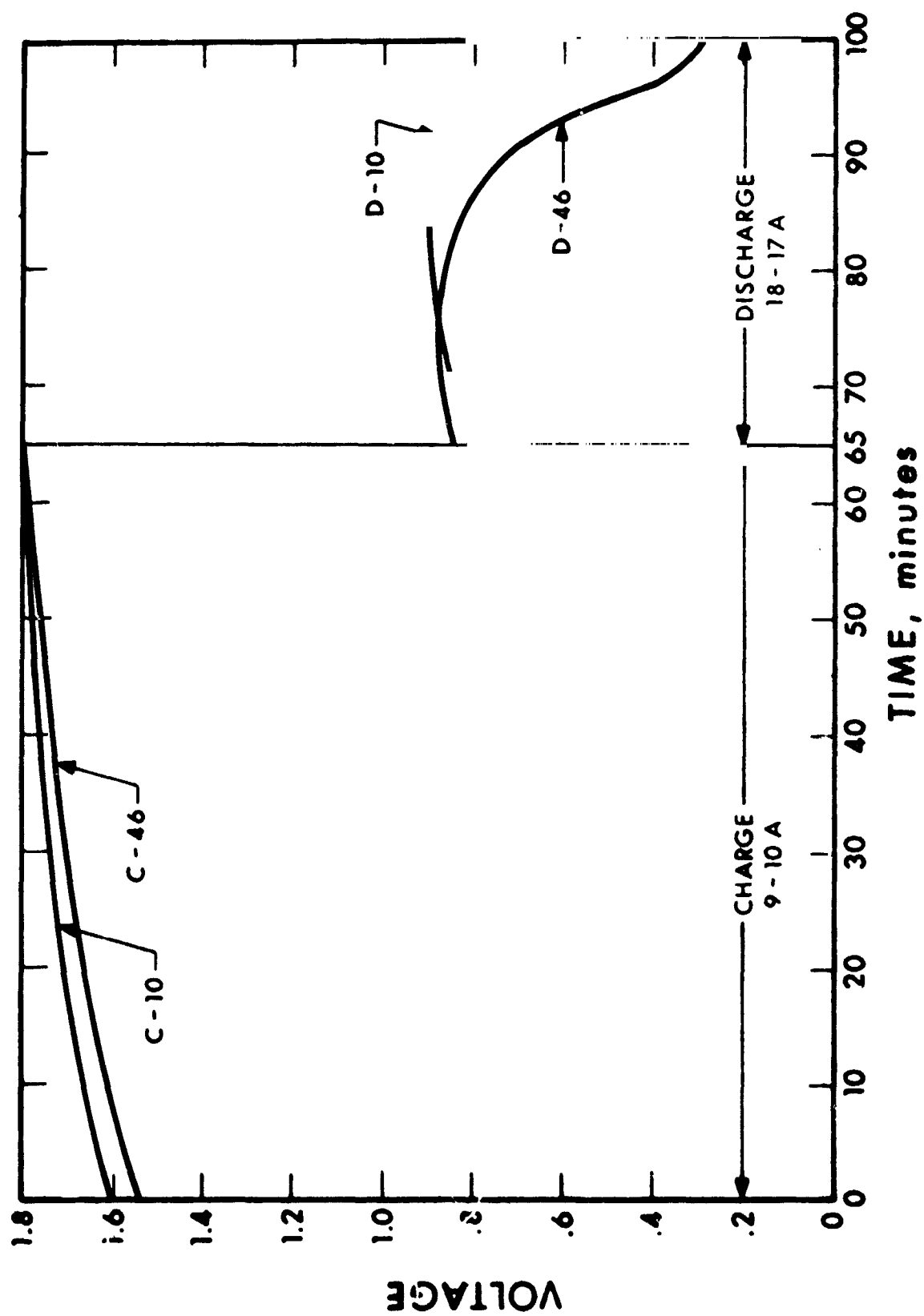


FIG. 3 CYCLING PERFORMANCE OF CELL 211

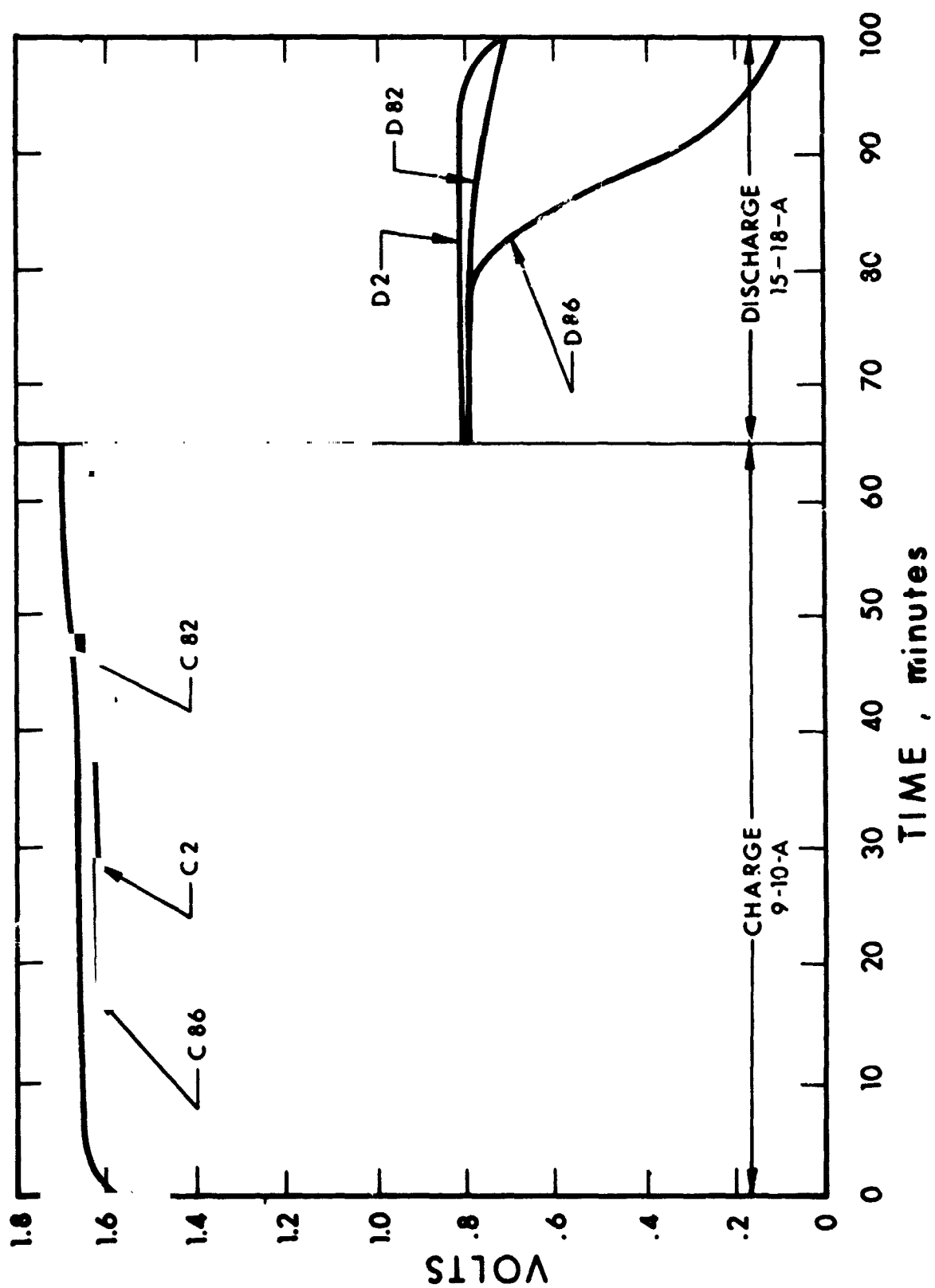


FIG. 4 CYCLING PERFORMANCE OF CELL 213

recombination during the charge cycle took place and the cell did not reach a full state of charge due to the gradual recombination. On subsequent discharges there was a rapid falloff in discharge voltage as the cell pressure dropped to levels of 50 psi and below. Cell 215 showed initial good performance, but on the 30th cycle it also developed a slow gas recombination, resulting in a falloff in the discharge voltage as the pressure decreased below 50 psi. The performance with the polypropylene potassium type matrices of the three above cells resulted in a gradual slow recombination after a period of cycling. The method of fabricating these matrices was apparently inadequate, and the resulting matrices had flaws or pinholes that developed with cycling. Additional attempts will be made to improve and perfect this type of matrix structure. Unfortunately, no conclusions could be drawn as to the ability of this type of matrix to increase cycle life and reduce degradation since long cycling periods were not achieved.

Cell 212 consisted of an American Cyanamid oxygen electrode that contained 40 milligrams of platinum per square centimeter (as opposed to the standard type electrodes which contain 9 milligrams of platinum per square centimeter). The matrix was 90 percent potassium titanate and 10 percent asbestos; the hydrogen electrode was the standard nickel porous plaque type. The cell was put on standard test cycle and subjected to 418 charge/discharge cycles. The voltage performance at various cycles is shown in Fig. 5. As can be seen, there was a gradual degradation in performance with cycling. In addition, this cell exhibited the slow gas recombination which resulted in a rapid falloff in the voltage performance during discharge in the latter cycles. The electrodes were removed from this cell unwashed and preassembled with a new matrix consisting of 90 percent potassium titanate and 10 percent asbestos. This new cell (designated 217) is still under test, and has shown good initial performance. It has undergone 30 cycles at this point.

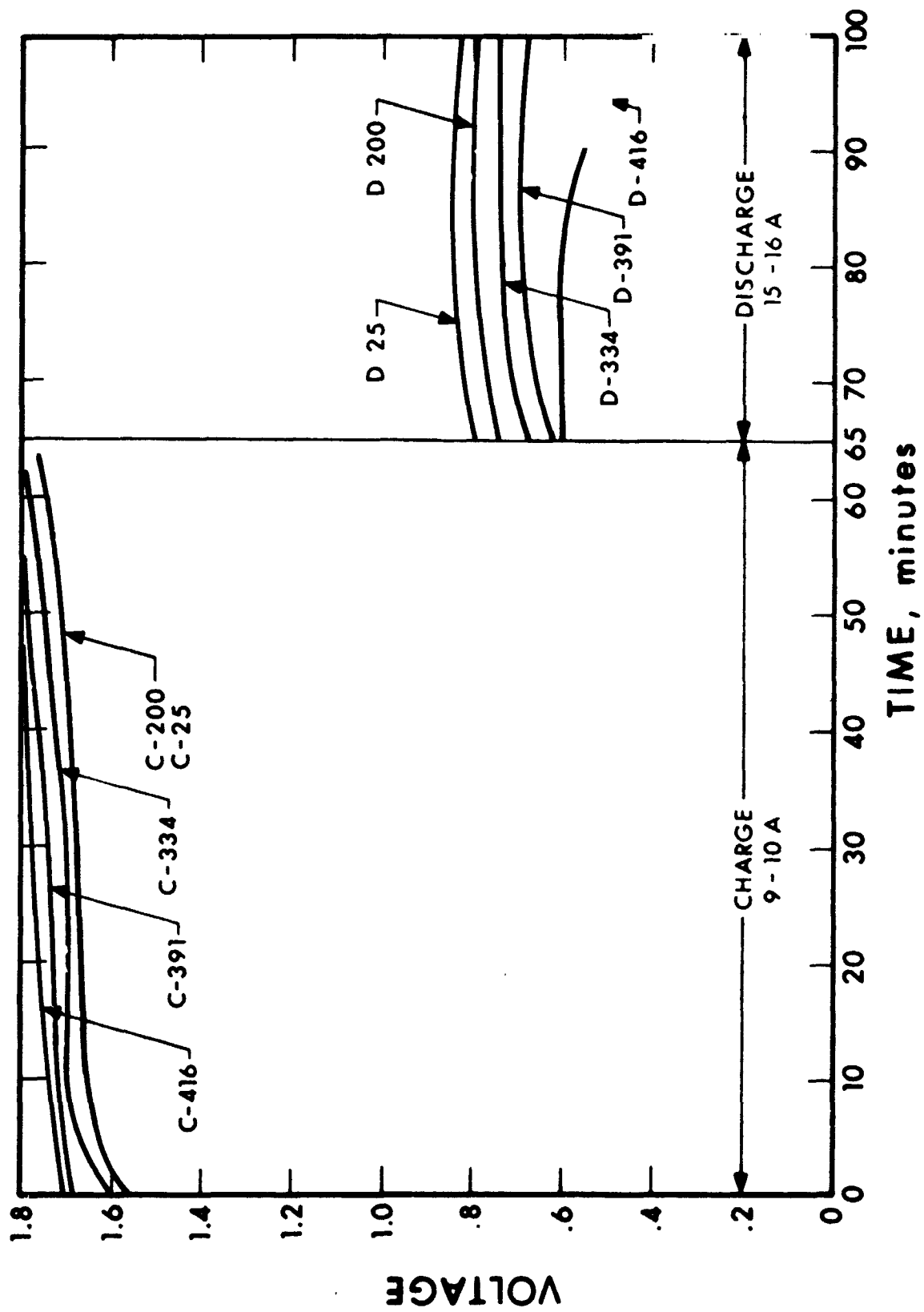


FIG. 5 CYCLING PERFORMANCE OF CELL 212

Cell 214 consisted of an American Cyanamid oxygen electrode and a porous nickel plaque hydrogen electrode with a matrix of 90 percent potassium titanate and 10 percent asbestos. This cell employed the oxygen electrode that had been used previously in cell 206. The hydrogen electrode was a new one since in disassembly the hydrogen electrode of cell 206 was damaged and could not be reused. The cell, still on test, has achieved 281 cycles. Figure 6 shows the voltage performance of the cell at various cycles. As can be seen, virtually no degradation has been observed at this point, and the cycling is continuing.

Cell 216 consisted of American Cyanamid electrodes of 9 milligrams platinum per square centimeter for both the hydrogen and oxygen electrodes and a matrix of 90 percent potassium titanate, 10 percent asbestos. The American Cyanamid electrode was employed on the hydrogen side to see if its use would improve performance and life. The cycling results are shown in Fig. 7. As can be seen, a gradual deterioration of charge and discharge voltage was observed. This rate of degradation was greater than that normally obtained with the nickel plaque hydrogen electrode cell. A new matrix will be placed in the cell to see if the electrodes are permanently affected.

From the results of single cells tested in this period, it appears that the oxygen electrodes are not affected or degraded by cycling with the potassium type asbestos matrices over periods of over 1000 accumulated cycles. However, there is unquestionably a degradation in performance with cycling that could be attributed to the hydrogen electrode or the matrix electrolyte composition. From the performance of the hydrogen concentration cell it appears that degradation is not due to the hydrogen electrode; it is most probably due to a matrix electrolyte reaction. For structural considerations, all matrices with long-life cells have been 10 percent asbestos by weight, and it is possible that this asbestos could be causing the problem. Additional attempts will be continued to fabricate a structurally sound matrix with materials that are more inert to the electrolyte than the asbestos seems to be.

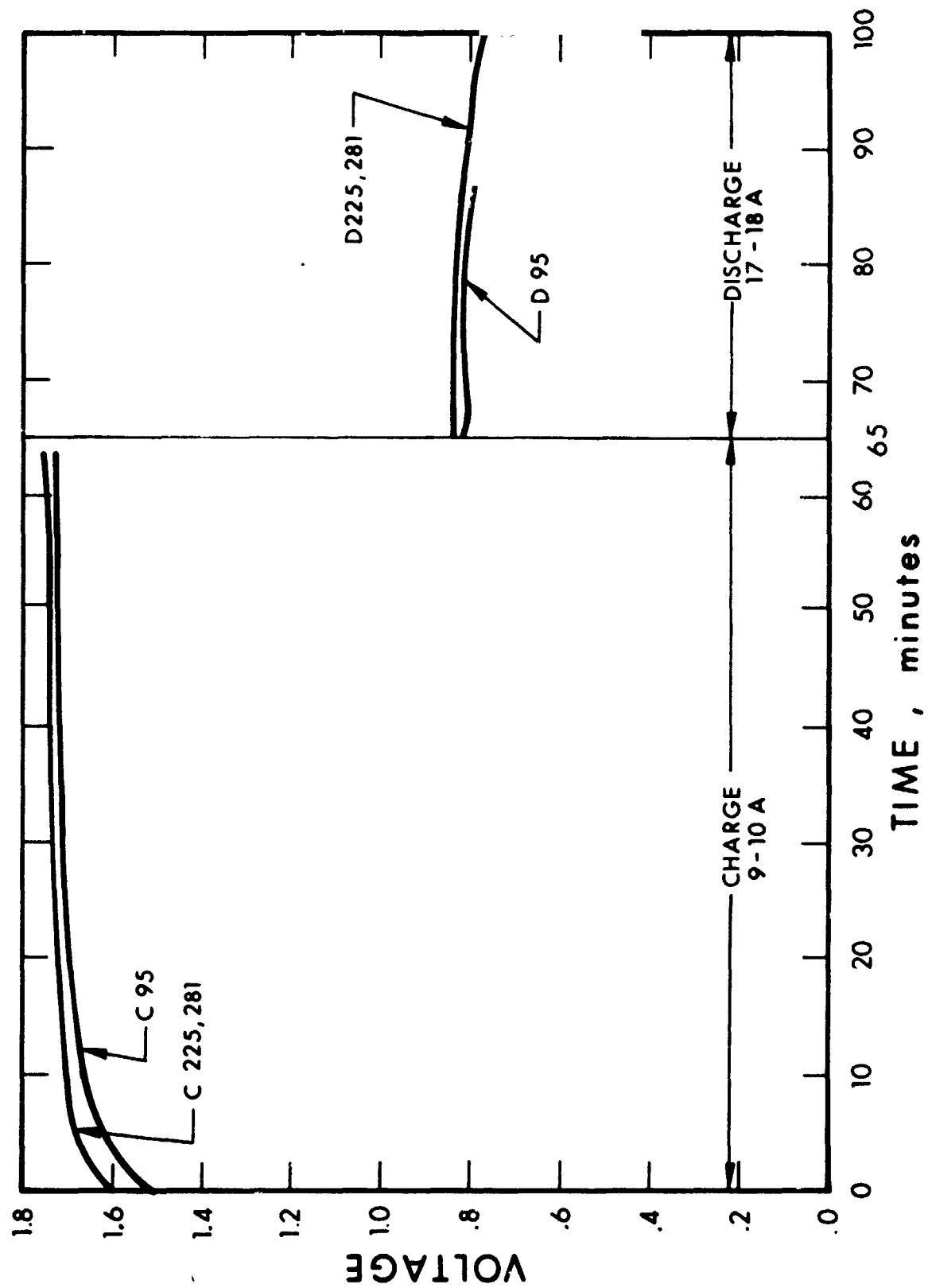


FIG. 6 CYCLING PERFORMANCE OF CELL 214

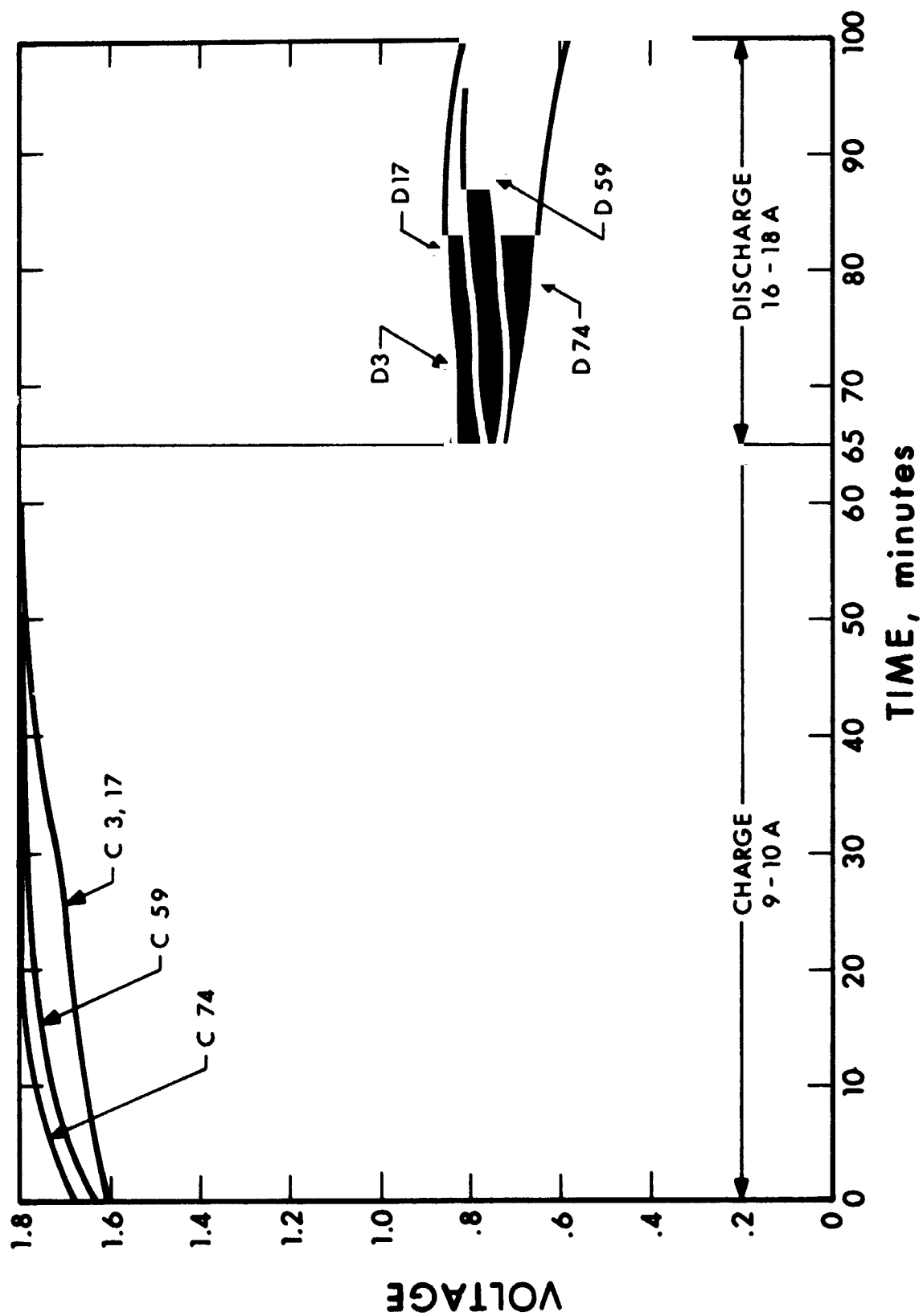


FIG. 7 CYCLING PERFORMANCE OF CELL 216

2.2 Potassium Titanate Analysis

In order to obtain a better understanding of the composition and impurities in the pigmentary potassium titanate used in the matrices, a sample was submitted to an outside testing laboratory for spectrographic analysis; the results are shown in Table II.

TABLE II

SPECTROGRAPHIC ANALYSIS OF PIGMENTARY POTASSIUM TITANATE

Titanium	47%	Aluminum	0.071%	Calcium	0.11%
Potassium	17%	Silicon	0.042%	Lead - less than	0.02%
Magnesium	0.020%	Other elements	- nil		

This analysis confirmed roughly the composition of potassium titanate as supplied by DuPont.

3. PLANS FOR NEXT PERIOD

Single cell tests will be continued to determine the component that is causing the deterioration in the potassium titanate cell configuration. Additional matrices will be evaluated containing mixes of potassium titanate and Teflon or polypropylene as substitute for asbestos fibers. The hydrogen concentration cell tests will be repeated to reproduce the test results. A six-cell unit employing American Cyanamid oxygen electrode 90-10 titanate asbestos mats and platinized nickel electrodes will be assembled and subjected to test. Additional corrosion tests will be set up to evaluate the rate of reaction of potassium titanate and potassium hydroxide.